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(21) International Application Number: PCT/US99/28995 (22) International Filing Date: 7 December 1999 (07.12.99) (30) Priority Data: 60/111,539 9 December 1998 (09.12.98) US (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): FOLEY, Peter, Robert [US/US]; 621 East Mehring Way, Apartment 906, Cincinnati, OH 45202 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).		(81) Designated States: CA, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: AQUEOUS LIQUID AUTOMATIC DISHWASHING DETERGENT COMPOSITION HAVING BROMINE AND CHLORINE BLEACH (57) Abstract An aqueous liquid automatic dishwashing detergent product having improved cleaning performance against starch based soil without a significant detrimental affect on protein based soil removal, and a process for achieving improved cleaning performance against starch based soil without a significant detrimental affect on protein based soil removal from dishware during automatic dishwashing are disclosed. The aqueous liquid automatic dishwashing detergent product comprises, by weight, a combination of hypochlorite bleaching species and hypobromite bleaching species. The bleaching species are present in an amount sufficient to deliver no greater than about 5 % by weight available halogen. The hypobromite bleaching species and the hypochlorite bleaching species are present in a molar ratio in a range of from about 1:1 to about 1:20, hypobromite bleaching species to hypochlorite bleaching species. The hypobromite bleaching species are generated from a water soluble bromide source. The water soluble bromide source is free of a water insoluble protective coating.		

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AQUEOUS LIQUID AUTOMATIC DISHWASHING DETERGENT COMPOSITION HAVING
BROMINE AND CHLORINE BLEACH

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TECHNICAL FIELD

The present invention relates to an aqueous liquid automatic dishwashing detergent composition. More particularly, the invention relates to an aqueous liquid automatic dishwashing detergent composition having a bromine and chlorine bleach system for delivering outstanding removal of starch based soil without any detrimental affect on the removal of protein based soil.

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BACKGROUND OF THE INVENTION

A key requirement of any liquid automatic dishwashing (ADW) detergent product is its ability to breakdown and remove dried, cooked on and burnt on soils from dishware, china, silverware, glassware and the like, referred generally hereinafter as dishware, for brevity. The soils that are typically deposited on such dishware include proteinaceous soils and starchy soils.

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While the ability of chlorine bleach based liquid dishwashing detergents to breakdown protein based soils is quite good and well documented in the art, the ability of chlorine bleach to breakdown certain starch based soils suffers from some limitations and thus leaves much room for improvement. In fact, because starch based soils are one of the key types of soils that consumers have to contend with in their quest for clean dishware, it has been an objective of the inventors to devise a composition that delivers a level of starch based soil removal which has heretofore been not possible, without detrimentally affecting the protein based soil removal.

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The performance of bromine bleach based liquid ADW composition in the removal of protein based soils is not so good and this inability of bromine bleach to remove protein based soils is also well documented in the art. However, the ability of bromine bleach in removal of starch based soils is impressive, particularly when the composition also has high alkalinity.

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In the past, it has also been recognized that as opposed to liquid ADW compositions, enzymes used in non-liquid detergents are effective against both protein based and starch based soil removal. However, enzyme based non-liquid detergents require an additional amount of time before an enzyme based detergent composition begins to operate at maximum efficiency. In the context of liquid ADW compositions, enzyme based liquid compositions are not stable in the presence of oxygen bleach. Enzyme based liquid ADW compositions are also incompatible with chlorine bleach and in general, it is safe to say that enzyme based liquid ADW compositions suffer from severe lack of enzyme compatibility with the chlorine and oxygen bleaching systems present in the liquid formulation.

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Other researchers in this field have also experimented with dual-bleach systems. Particularly, the use of dual bleach systems, such as chlorine and bromine bleaches is known in the art. However, it has heretofore been understood by those skilled in the art, that to use a bromine bleach in conjunction with a chlorine bleach in a liquid ADW composition, the source of the bromine bleach has to be substantially insoluble in water or at the very least sparingly soluble in water. It has been heretofore understood that a water soluble bromine bleach source must be coated with a water insoluble coating, which dissolves only at higher temperatures, such as above 100 degrees F, which are commonly encountered in the wash solution. It has heretofore been understood by those skilled in the art that the hypobromite bleaching species must be generated in the wash solution only and that any "in situ" generation of hypobromite, i.e., generation of active hypobromite in the liquid ADW product is detrimental to the storage stability of the liquid ADW product.

The inventor of the subject invention has surprisingly discovered that there is no need that the bromine source be water-insoluble or water-insoluble. The inventor of the subject invention has also discovered that if a water-soluble bromine source is used, such as alkali and alkaline earth metal bromides, it is no longer essential that such a water-soluble bromine source be coated with a water-insoluble coating which melts only at the temperature in the wash solution of the automatic dishwashing machine. This critical discovery has simplified that formulation of dual bleach systems, which can now use water-soluble bromine sources without any coating, a feature heretofore believed to be impossible to attain without sacrificing the liquid ADW product stability. This has enabled the formulation of dual bleach aqueous liquid ADW products that offer improved starch removal performance across all temperature ranges encountered in an automatic dishwasher, even when cold water is used.

It has thus been extremely desirable to have a thixotropic aqueous liquid automatic dishwashing detergent composition that not only delivers outstanding removal of starch based soil without any detrimental affect on protein based soil removal, but is importantly, stable in storage. When a dual bleach system using hypobromite and hypochlorite bleaching species is used, it has very much been desirable to have a thixotropic aqueous liquid automatic dishwashing detergent composition that not only does not require the source of hypobromite bleaching species to be water-insoluble or water-sparingly soluble in order to be stable. It has been desirable to have a liquid ADW product using a dual bleach system of bromine and chlorine bleaching species wherein there is no need to coat a water-soluble bromine bleach source with a water-insoluble coating that melts at the temperature in excess of 100 degrees F. It has also been desirable to have a stable thixotropic aqueous liquid automatic dishwashing detergent composition wherein

the hypobromite bleaching species is generated "in situ" in the liquid ADW product itself, thus allowing for better colder temperature, i.e., temperatures less than 100 degree F, starch removal performance of the liquid ADW product.

5 The inventor of the subject invention has discovered that the above problem is solved by formulating an aqueous liquid ADW composition that utilizes a unique combination of hypochlorite bleach and hypobromite bleach in a pre-selected ratio, wherein the bromine source is water-soluble. The aqueous liquid ADW composition of the present invention delivers excellent removal of starch based soil and without any detrimental affect on protein based soil removal. Because the hypobromite bleaching species is generated "in situ", i.e., in the liquid
10 ADW product itself, the starch removal performance of the liquid ADW product is immediate and improved even at temperature less than 100 degrees F as compare to those liquid ADW products wherein water-insoluble, water-sparingly soluble, or water-soluble-but-coated bromine sources are used.

Thus the present invention aims to solve all of the aforementioned problems.

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BACKGROUND ART

U.S. Patent No. 5,164,106 discloses a non-aqueous liquid automatic dishwasher detergent composition containing a dual bleach system.

U.S. Patent No. 5,108,641 discloses an aqueous liquid automatic dishwasher detergent composition containing a dual bleach system.

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SUMMARY OF THE INVENTION

The invention meets the needs above by providing an aqueous liquid automatic dishwashing detergent product having improved cleaning performance against starch based soil without a significant detrimental affect on protein based soil removal, and a process for achieving improved cleaning performance against starch based soil without a significant detrimental affect
25 on protein based soil removal from dishware during automatic dishwashing.

In one aspect of the present invention, the aqueous liquid automatic dishwashing detergent product comprises, by weight, a combination of hypochlorite bleaching species and hypobromite bleaching species. The bleaching species are present in an amount sufficient to deliver no greater than about 5% by weight available halogen. The hypobromite bleaching
30 species and the hypochlorite bleaching species are present in a molar ratio in a range of from about 1:1 to about 1:20, hypobromite bleaching species to hypochlorite bleaching species. The hypobromite bleaching species are generated from a water soluble bromide source. The water soluble bromide source is free of a water insoluble protective coating.

In another aspect of the present invention, the process comprises the steps of (a) providing an aqueous liquid automatic dishwashing detergent composition as set forth above, and (b) washing the dishware by an automatic dishwashing method.

The aqueous liquid automatic dishwashing detergent product of the present invention not only delivers outstanding removal of starch based soil without any detrimental affect on protein based soil removal, but is importantly, stable in storage, despite the generation of the hypobromite bleaching species "in situ" in the liquid product.

DETAILED DESCRIPTION OF THE INVENTION

In the preferred embodiment of the present invention, the aqueous liquid automatic dishwashing detergent product comprises, by weight, a combination of hypochlorite bleaching species and hypobromite bleaching species. The bleaching species are present in an amount sufficient to deliver no greater than about 5% by weight available halogen. The hypobromite bleaching species and the hypochlorite bleaching species are present in a molar ratio in a range of from about 1:1 to about 1:20, hypobromite bleaching species to hypochlorite bleaching species. The hypobromite bleaching species are generated from a water soluble bromide source. The water soluble bromide source is free of a water insoluble protective coating.

The mole ratio of the bromide to available chlorine is critical and is desirable in a range of from about 1:1 to about 1:20, more desirable in a range of from about 1:2 to about 1:7, preferably in a range of from about 1:2 to about 1:6, more preferably in a range of from about 1:3 to about 1:6 and most preferably, about 1:4, hypobromite bleaching species to hypochlorite bleaching species.

In accordance with the present invention, the aqueous liquid automatic dishwashing detergent product is prepared by incorporating a water soluble source of hypobromite bleaching species in a dishwasher composition containing a hypochlorite bleaching species.

Thixotropic cleaning compositions are highly viscous in a quiescent state and have relatively high yield stress values. When subjected to shear stresses, however, such as being shaken in a container or squeezed through an orifice, they quickly fluidize and upon cessation of the applied shear stress, quickly revert to a high viscosity state. The thixotropic aqueous liquid ADW compositions are low foaming, they are readily soluble in the washing medium and most effective at pH values best conducive to improved cleaning performance, such as in a range of desirably from about pH 9.0 to about pH 13.0, preferably from about pH 9.0 to about pH 12.0.

The thickness or viscosity of the liquid product may be altered by the addition of a fatty acid, metal salt of a fatty acid and/or clay thixotropic thickener. Desirably, about 0.02% to about 3% by weight of a fatty acid.thixotropic thickener is added to the liquid detergent

composition. Alternatively, in addition to about 0.02% to about 3% by weight of a fatty acid thixotropic thickener, from about 0.1% to about 3% of an inorganic thixotropic clay thickener may be also be added to the liquid detergent composition. Still alternatively, the aqueous liquid detergent composition may include from about 1.5% to about 8% of a fatty acid thixotropic thickener.

In a preferred embodiment of the invention, the physical stability of the liquid product may be improved and the thickness of the liquid product may be altered by the addition of a cross linking polyacrylate thickener to the liquid detergent product as a thixotropic thickener. The polyacrylate thickener is added in an amount sufficient to achieve a yield stress in a range of from about 10 Pa to about 30 Pa and a static viscosity of at least 5000 l.s⁻¹. The aqueous thixotropic liquid automatic dishwashing detergent product exhibits rheological properties are evaluated by testing product viscosity as a function of shear rate. The compositions exhibit higher viscosity at a low shear rate and lower viscosity at a high shear rate. In practical terms, this means improved pouring and processing characteristics as well as less leaking in the machine dispenser-cup, compared to prior liquid or gel ADW compositions. In terms of apparent viscosity, it has been ascertained that so long as the viscosity at room temperature (22 °C ± 1°C) measured in a Brookfield Viscosimeter HATD, using a number 4 spindle at 20 rpm, is in a range of about 20,000 to about 30,000 cps, depending upon the formula and the thickener used, the composition can be readily shaken so that a thixotropic composition can be easily "fluidized" or "liquefied" to allow the product to be dispensed through a conventional squeeze tube bottle or other convenient dispenser.

The present invention is based upon the surprising discovery that outstanding removal of starch based soil without any detrimental affect on protein based soil removal can be attained by adding to the thixotropic aqueous liquid detergent composition, hyprobromite bleaching species and hypochlorite bleaching species in a molar ratio of hyprobromite:hypochlorite in a range of from about 1:1 to about 1:20. The physical stability, i.e., resistance to phase separation and settling, is improved by adding to the composition, a small effective amount of a thixotropic thickener and stabilizing agent, such as the crosslinked polyacrylate thickener as mentioned before. Further, the liquid product is stable despite the generation of the hyprobromite species in situ, rather than in the wash solution of the automatic dishwashing machine, and despite the water soluble nature of the bromide source, and further despite the fact that the water soluble bromide source is not encapsulated, either fully or partially, or enclosed in any manner, by a water insoluble protective coating or barrier.

Hypochlorite Bleaching Species

Hypochlorite generating compounds suitable for use in the compositions of the present invention are those water soluble dry solid materials which generate hypochlorite ion on contact with, or dissolution in, water. The preferred hypochlorite compounds are alkali and alkaline earth hypochlorites. The hypochlorite generating compounds are generally soluble in the product composition. Examples thereof are the dry, particulate heterocyclic N-chlorimides such as trichlorocyanuric acid, dichlorocyanuric acid and salts thereof such as sodium dichlorocyanurate and potassium dichlorocyanurate. The corresponding dichloroisocyanuric and trichloroisocyanuric acid salts can also be used. Other N-chloroimides may be used such as N-chlorosuccinimide, N-chloromalanimide, N-chlorophthalimide and N-chloronaphthalimide. Additional suitable N-chloroimides are the hydantoin such as 1,3-dichloro-5,5-dimethylhydantoin; N-monochloro-C,C-dimethylhydantoin; methylene-bis (N-chloro-C,C-dimethylhydantoin); 1,3-dichloro-5-methyl-5-isobutylhydantoin; 1,3-dichloro-5-methyl-5-ethylhydantoin; 1,3-dichloro-5,5-diisobutylhydantoin; 1,3-dichloro-5-methyl-5-n-amylhydantoin; and the like. Other useful hypochlorite-liberating agents are trichloromelamine and dry, particulate, water soluble anhydrous inorganic salts such as lithium hypochlorite and calcium hypochlorite. The hypochlorite liberating agent may, if desired, be a stable, solid complex or hydrate such as sodium p-toluene-sulfo-chloramine-trihydrate (chloramine-T), sodium benzene-sulfo-chloramine-dihydrate, calcium hypochlorite tetrahydrate, or chlorinated trisodium phosphate containing no more than 4% available chlorine produced by combining trisodium phosphate in its normal $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ form and an alkali metal hypochlorite (e.g., sodium hypochlorite).

In the preferred embodiment of the present invention, the hypochlorite bleaching species are present in a sufficient amount of deliver in a range of 0.5% to 4% by weight, available chlorine. Specific amounts of the desired hypochlorite species can be determined by one skilled in the art without undue experimentation to attain the aforementioned available chlorine. For example, a composition containing about 7.4 to 22.20% by weight of sodium hypochlorite contains about 1 to 3% by weight of available chlorine.

Desirably the proportion of chlorine-liberating compound employed will be such as to yield a product which contains desirably no more than 4% available chlorine.

Hypobromite Bleaching Species

The present invention hinges on the important discovery that the bromide compounds that can be used in accordance with the present invention are those that are water soluble. The invention expressly precludes the need for water insoluble or only sparingly water soluble bromide compounds that are soluble in the larger volume of the dishwasher wash solution at wash temperatures of 100 °F to 140 °F. It is expressly preferred, for the sake of simplicity and

economy, that the water soluble bromide compounds are free of a protective water-insoluble coating of any form or manner.

Water soluble bromide salts are best suited for aqueous liquid ADW compositions because they result in a stable to storage liquid product despite the formation of the active hypobromite in the detergent liquid product generated in situ therein, rather than in the wash cycle at higher temperature and increased water volume in the dishwasher. It has been discovered that bromide salts that are soluble in the aqueous liquid ADW product can be used and they do not degrade the shelf life of the liquid ADW product.

In the preferred embodiment of the invention, readily water soluble bromide compounds, such as alkali and alkaline earth metal bromides are used. Preferably, sodium bromide is used. These readily soluble bromide compounds are preferably not encapsulated in a protective coating that is insoluble or only sparingly soluble in the liquid product. Thus, a balanced aqueous liquid detergent product is obtained which contains an effective amount of the bromide which reacts with the hypochlorite to form a sufficient amount of hypobromite to remove the starchy carbohydrate soil and leaves a sufficient amount of hypochlorite ion in the wash bath to remove the proteinaceous soil. Thus, the aforementioned weight percent available halogen and the mole ratio of bromide to available chloride are important features of the present invention.

Thixotropic Thickeners

The thixotropic thickeners or suspending agents that can be used in accordance with the present invention to provide the aqueous medium with thixotropic properties may be organic, for example, fatty acid or fatty acid metal salts or inorganic colloid forming clay materials. The thixotropic thickeners should be stable to high alkalinity and stable to chlorine bleach compounds such as sodium hypochlorite. The useful thixotropic thickeners comprise the fatty acids, the fatty acid polyvalent metal salts and the inorganic, colloid-forming clays of smectite and/or attapulgite types. Thus, examples of the fatty acids which can be used as thickeners include, for example, decanoic acid, lauric acid, dodecanoic acid, palmitic acid, myristic acid, stearic acid, oleic acid, eicosanoic acid, tallow fatty acid, coco fatty acid, soya fatty acid and mixtures of these acids. Stearic acid and mixed fatty acids, e.g. coco fatty acid, are also useful. There may also be used in the present invention the conventional inorganic thixotropic clay thickeners. The clay thickeners may be used in small amounts in combination with the fatty acid thickeners or in combination with fatty acid polyvalent metal salt thickeners. The clay thickeners, however, may be used by themselves as the thixotropic thickeners. Useful clay thickeners comprise the inorganic, colloid forming clays of smectite and/or attapulgite types. Smectite clays include montmorillonite (bentonite), hectorite, attapulgite, smectite, saponite, and

the like. Montmorillonite clays are also useful and are available under tradenames such as Thixogel (Registered Trademark) No. 1 and Gelwhite (Registered Trademark) GP, H, etc., from Georgia Kaolin Company; and Eccagum (Registered Trademark) GP, H, etc., from Luthern Clay Products.

- 5 In a preferred embodiment of the invention, the thickener used is a cross linking polyacrylate thickener, added to the liquid detergent product. The polyacrylate thickener is added in an amount sufficient to achieve a yield stress in a range of from about 10 Pa to about 30 Pa and a static viscosity of at least 5000 l.s⁻¹.

pH adjusting components

- 10 It is preferred herein that the pH at about 1% dilution with de-ionized water, by weight, of the aqueous thixotropic liquid ADW composition product be at least about 9.0, more preferably from about 10.5 to 12.0 and most preferably at least about 11.7. The pH adjusting components are desirably selected from sodium or potassium carbonate or sesquicarbonate, sodium or potassium citrate, citric acid, sodium or potassium bicarbonate, sodium or potassium borate, sodium or
15 potassium hydroxide, and mixtures thereof. NaOH is a preferred ingredient for increasing the pH to within the above ranges. Other preferred pH adjusting ingredients are potassium hydroxide, potassium silicate, sodium silicate, sodium carbonate, potassium carbonate, and mixtures thereof.

Low Foaming Non-ionic Surfactant

- The liquid nonionic surfactant detergents that can be used to practice the present invention are
20 preferably chlorine bleach stable low foaming non-ionic surfactants. In the preferred embodiment, such surfactants are present in a range of from about 0.1% to about 10% by weight of the liquid composition. The chlorine bleach stable low foaming nonionic surfactants are desirably selected from the group consisting of chloride bleach stable alkoxylated alcohols, and mixtures thereof. Such surfactants are generally known to one skilled in the art and need not be
25 elaborated here, for purposes of brevity.

Other ingredients

- The aqueous liquid automatic dishwashing detergent composition optionally also contains from about 0.5% to about 20% of a dispersant polymer selected from the group consisting of polyacrylates and polyacrylate copolymers, and from about 0.1% to about 5% of a chlorine
30 bleach stable foam suppressant. Such foam suppressants are well known to those skilled in the art.

In an embodiment of the invention an aqueous liquid concentrate automatic dishwashing detergent composition is formulated using the below named ingredients, as set forth in Example A.

EXAMPLE A

	<u>Ingredient</u>	<u>weight % active</u>
	Sodium Tripolyphosphate	17.50
	Sodium Silicate	5.16
5	Potassium hydroxide	3.58
	Sodium hydroxide	1.95
	Polyacrylate polymer	1.01
	Nitric Acid	0.0117
	Perfume	0.03
10	Sodium Silicate	0.95
	Sodium Benzoate	0.75
	Sodium hypochlorite	1.15
	Sodium Bromide	0.80
	Water	Balance
15	TOTAL	100.00

Accordingly, having thus described the invention in detail, it will be obvious to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.

WHAT IS CLAIMED IS:

1. An aqueous liquid automatic dishwashing detergent product having improved cleaning performance against starch based soil without a significant detrimental affect on protein based soil removal, characterized by, by weight:
 - (a) a combination of hypochlorite bleaching species and hypobromite bleaching species, said bleaching species being present in an amount sufficient to deliver no greater than 5% by weight available halogen;
 - (b) said hypobromite bleaching species and said hypochlorite bleaching species being present in a molar ratio in a range of from 1:1 to 1:20, hypobromite bleaching species to hypochlorite bleaching species;
 - (c) said hypobromite bleaching species being generated from a water soluble bromide source; and
 - (d) said water soluble bromide source being free of a water insoluble protective coating.
2. An aqueous liquid detergent product according to claim 1, wherein said hypochlorite bleaching species is selected from the group consisting of chlorocyanurates, chloroisocyanurates, dichloroisocyanurates, and alkali and alkaline earth metal hypochlorites.
3. An aqueous liquid detergent product according to claims 1-2, wherein said hypochlorite bleaching species is selected from the group consisting of alkali and alkaline earth metal hypochlorites.
4. An aqueous liquid detergent product according to claims 1-3, wherein said water soluble bromide source is selected from the group consisting of alkali and alkaline earth metal bromides.
5. An aqueous liquid detergent product according to claims 1-4, wherein said hypobromite bleaching species is generated in situ in said aqueous liquid detergent product.
6. An aqueous liquid detergent product according to claims 1-5, wherein said water soluble bromide source of said hypobromide bleaching species is sodium bromide.

7. An aqueous liquid detergent product according to claims 1-6, wherein said hypobromite bleaching species and said hypochlorite bleaching species are present in a molar ratio in a range of from 1:2 to 1:6, hypobromite bleaching species to hypochlorite bleaching species.
8. An aqueous liquid detergent product according to claims 1-7, wherein said hypobromite bleaching species and said hypochlorite bleaching species are present in a molar ratio in a range of from 1:3 to 1:6, hypobromite bleaching species to hypochlorite bleaching species.
9. An aqueous liquid detergent product according to claims 1-8, including a pH adjusting component, wherein said pH adjusting component is selected from the group consisting of sodium or potassium carbonate or sesquicarbonate, sodium or potassium citrate, citric acid, sodium or potassium bicarbonate, sodium or potassium borate, sodium or potassium hydroxide, and mixtures thereof.
10. A process for achieving improved cleaning performance against starch based soil without a significant detrimental affect on protein based soil removal from dishware during automatic dishwashing, characterized by the steps of:
 - (a) providing an aqueous liquid automatic dishwashing detergent product according to claim 1; and
 - (b) washing said dishware by an automatic dishwashing method.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/28995

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D3/395

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 108 641 A (AHMED FAHIM U ET AL) 28 April 1992 (1992-04-28) cited in the application examples 1-6 claims 1-16	1-10
X	WO 97 20909 A (PETRI MARCO ;NA HENRY CHENG (US); PROCTER & GAMBLE (US)) 12 June 1997 (1997-06-12) examples 1-7	1-9
X	US 4 755 354 A (TRINH TOAN ET AL) 5 July 1988 (1988-07-05) column 2, line 38 -column 3, line 22 column 5, line 17 - line 22	1-9
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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P,X	WO 99 06320 A (NALCO CHEMICAL CO) 11 February 1999 (1999-02-11) claims 1-7 ---	1-9
A	EP 0 186 234 A (PROCTER & GAMBLE) 2 July 1986 (1986-07-02) claims 1-16 ---	1-10
A	EP 0 395 186 A (COLGATE PALMOLIVE CO) 31 October 1990 (1990-10-31) claims 1-14 -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/28995

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(12) **United States Patent**
Hahn(10) **Patent No.:** **US 6,622,736 B1**
(45) **Date of Patent:** **Sep. 23, 2003**(54) **WATER-SOLUBLE GLASS AS CORROSION
PROTECTION FOR GLASSWARE IN A
DISHWASHING MACHINES**(75) **Inventor:** **Karlheinz Hahn, Otterstadt (DE)**(73) **Assignee:** **Reckitt Benckiser N.V., Hoofddorp
(NL)**(*) **Notice:** Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.(21) **Appl. No.:** **09/868,478**(22) **PCT Filed:** **Dec. 29, 1999**(86) **PCT No.:** **PCT/EP99/10467**

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(2), (4) **Date:** **Aug. 15, 2001**(87) **PCT Pub. No.:** **WO00/39259****PCT Pub. Date:** **Jul. 6, 2000**(30) **Foreign Application Priority Data**

Dec. 29, 1998 (DE) 198 60 670

(51) **Int. Cl.⁷** **B08B 9/20**(52) **U.S. Cl.** **134/25.2; 134/25.1; 134/25.4;
134/42; 510/220; 510/224; 510/232; 510/233**(58) **Field of Search** **134/25.2, 42, 25.1,
134/25.4; 510/220, 224, 232, 233**(56) **References Cited****U.S. PATENT DOCUMENTS**3,677,820 A * 7/1972 Rutkowski 134/25.2
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Abstract: JP 63-308100 (Dec. 16, 1988).

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Primary Examiner—Randy Gulakowski*Assistant Examiner*—M. Kornakov(74) *Attorney, Agent, or Firm*—Akin Gump Strauss Hauer
& Feld, L.L.P.(57) **ABSTRACT**A water soluble glass is used in dishwashing machines as
corrosion protection for glassware. The water soluble glass
consists of at least one compound which, in the cleaning
and/or rinsing cycles, releases an agent that protects glass-
ware against corrosion. Each of the compounds accounts for
no more than 85 molar % of the glass and the solubility of
the water soluble glass is defined by a mass loss of at least
0.5 mm under the conditions specified in DIN ISO 719.**26 Claims, No Drawings**

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WATER-SOLUBLE GLASS AS CORROSION PROTECTION FOR GLASSWARE IN A DISHWASHING MACHINES

BACKGROUND OF THE INVENTION

The invention relates to a new type of use for a water-soluble glass to protect glassware from corrosion during washing and/or rinsing cycles of a dishwashing machine, compositions intended for use in a dishwashing machine for the aforesaid purpose and a method of inhibiting the corrosion of glassware during washing and/or rinsing cycles of a dishwashing machine.

The problem of glassware corroding during washing and/or rinsing cycles of a dishwashing machine has long been known. Current opinion is that the problem of corrosion in glassware is the result of two separate phenomena. On the one hand, the corrosion is clearly due to minerals escaping from the glass composition accompanied by hydrolysis of the silicate network. On the other hand, silicate material is released from the glass. After several washes in a dishwashing machine, both phenomena can cause damage to glassware such as cloudiness, scratches, streaks and similar.

Silicate compounds are known to be effective in preventing minerals from being released from the glass composition but on the other hand can tend to increase the separation of silicate material at the surface of the glass.

Various proposals have been put forward as a means of dealing with the problems described above.

One approach is to use zinc, either in metallic form (U.S. Pat. No. 3,677,820) or in the form of zinc compounds. The use of soluble zinc salts as a means of preventing the corrosion of glassware in dishwasher detergents is described in U.S. Pat. No. 3,255,117, for example.

Because of a number of disadvantages inherent in using soluble zinc salts (in particular the formation of a precipitate of insoluble zinc salts with other ions in the washing or rinsing water), European patent applications EP 0 383 480, EP 0 383 482 and EP 0 387 997 propose the use of insoluble zinc compounds as a means of inhibiting the corrosion of glassware in automatic dishwashing machines. Specifically, the insoluble zinc salts proposed are zinc silicate, zinc carbonate, zinc oxide, basic zinc carbonate (approximately: $\text{Zn}_2(\text{OH})_2\text{CO}_3$), zinc hydroxide, zinc oxalate, zinc monophosphate ($\text{Zn}_3(\text{PO}_4)_2$) and zinc pyrophosphate ($\text{Zn}_2(\text{P}_2\text{O}_7)$). When using zinc salts of this type in granular cleansing compounds, the insoluble zinc compound is specified as having a maximum particle size of less than 1.7 mm (EP 0 383 482), whilst a mean particle size of less than 250 μm is specified for the insoluble zinc compound used in a liquid dishwasher compound (EP 0 383 480 and EP 0 387 997).

The disadvantage of this prior art essentially resides in the fact that, because the zinc compounds are not readily soluble or are insoluble, it is difficult to ensure that a sufficient quantity of active agent will always be present in the washing or rinsing liquid to protect glassware from corrosion. Furthermore, in view of the high specific density of the insoluble zinc compounds listed, problems of separation arise with powdered mixtures or settlement in the case of liquid mixtures.

Finally, all of the known compositions are intended to be active during only one specific stage of the washing cycle, i.e. if admixed with a granular detergent composition during

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the washing cycle or if admixed with a liquid rinsing composition with the rinsing cycle. None of the known compositions has the capacity to become and remain active starting from the pre-wash cycle and/or one of the intermediate rinsing cycles onwards.

The underlying objective of the present invention is to resolve at least one, but preferably all of the existing problems outlined above.

SUMMARY OF THE INVENTION

This objective is achieved by the invention due to the use of a water-soluble glass to protect glassware from corrosion, the water-soluble glass being made from at least one compound which releases an active anti-corrosion agent during the washing and/or rinsing cycles of a dishwashing machine, each of these compounds accounting for no more than 85 molar % of the glass and the solubility of the water-soluble glass being defined by a mass loss of at least 0.5 mg under the conditions specified in DIN ISO 719.

By preference, the solubility of the water-soluble glass is such that the mass loss under the specified conditions is at least 10 mg, more preferably at least 50 mg.

The invention additionally proposes that the compound(s) which release(s) an active agent to protect glassware from corrosion during the washing and/or rinsing cycles of a dishwashing machine should be from the group consisting of the oxides of zinc, aluminium, tin, magnesium, calcium, strontium, titanium, zirconium, manganese and/or lanthanum and/or precursors thereof.

In one particular embodiment, the invention proposes that at least one of the compounds used should be zinc oxide and/or a precursor thereof.

By preference, at least one of the glass-forming components of the water-soluble glass is phosphorus pentoxide and/or a precursor thereof.

Also particularly preferred as a glass component(s) is (are) one or more alkali metal oxides and/or precursors thereof.

In one especially preferred embodiment, the invention proposes using the water-soluble glass in the form of a tablet, the tablet preferably being made by casting or drawing the water-soluble glass.

Alternatively, the water-soluble glass is used in crushed form, either in the form of glass platelets or in around form.

In ground form, the mean particle size is preferably at most 500 μm .

The invention additionally relates to a composition for use in a dishwashing machine, containing an active quantity of a water-soluble glass in crushed form to protect glassware from corrosion, the water-soluble glass being made from at least one compound which releases an active agent to protect glassware from corrosion during washing and/or rinsing cycles of a dishwashing machine, each of these compounds accounting for at most 85 molar % of the glass and the solubility of the water-soluble glass being defined by a mass loss of at least 0.5 mg under the conditions specified in DIN ISO 719.

The water-soluble glass is preferably used either in the form of thin glass platelets or in ground form, most preferably with a mean particle size of at most 500 μm .

The composition proposed by the invention contains the water-soluble glass in a quantity of from 0.1 to 10.0% by weight, more preferably from 0.5 to 5.0% by weight.

In an alternative embodiment, the invention proposes a composition for use in a dishwashing machine, character-

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ized in that it contains an active quantity of a water-soluble glass tablet form to protect glassware from corrosion, the water-soluble glass being made from at least one compound which releases an active agent to protect glassware from corrosion during washing and/or rinsing cycles of a dishwashing machine, each of these compounds accounting for at most 85 molar % of the glass and the solubility of the water-soluble glass being defined by a mass loss of at least 0.5 mg under the conditions specified in DIN ISO 719.

The tablet proposed by the invention is preferably made by casting or drawing the water-soluble glass.

With both the composition in which the water-soluble glass is present in crushed form and in the embodiment where the water-soluble glass is provided as a tablet, the solubility of the water-soluble glass is such that the mass loss under the specified conditions is preferably at least 10 mg, more preferably at least 50 mg.

In both cases, the compound(s) which release(s) an active agent to protect glassware from corrosion during washing and/or rinsing cycles of a dishwashing machine is (are) from the group consisting of the oxides of zinc, aluminium, tin, magnesium, calcium, strontium, titanium, zirconium, manganese and/or lanthanum and/or precursors thereof.

In one particular embodiment, the invention proposes that at least one of the compounds should be zinc oxide and/or a precursor thereof.

Preferably, at least one of the glass-forming components of the water-soluble glass is phosphorus pentoxide and/or a precursor thereof.

One or more alkali metal oxides and/or precursors thereof may also be used as glass component(s).

The invention additionally relates to a method of inhibiting the corrosion of glassware in washing and/or rinsing cycles of a dishwashing machine by bringing the glassware into contact with washing and/or rinsing water containing an active quantity of a composition containing the water-soluble glass in ground form.

Alternatively, a composition as proposed by the invention is prepared in the form of a tablet, placed in the interior of the dishwasher at a point which is accessible to the washing and/or rinsing water.

Before giving a detailed explanation of the features and advantages of the present invention, it should be pointed out that for the purpose of the present invention, the concept "glass" should be construed as meaning not only glass in the narrower sense, i.e. an amorphous, non-crystalline, transparent substance produced by hardening a melt, but also that produced by hardening a melt which has crystalline inclusions in an amorphous glass matrix.

DETAILED DISCLOSURE

The present invention solves at least one and, in preferred embodiments, all the problems inherent in the prior art described above in a surprisingly simple manner.

By using a water-soluble glass as a "base" for one or more reagents to protect glassware from corrosion in a dishwasher, the problems caused by the extensive formation of precipitate from insoluble salts which result in an undesirable deposit, such as occurs with the prior art in particular due to the use of soluble zinc salts for this purpose, are avoided. Instead, the active agents, such as zinc ions, for example, are released from the water-soluble glass proposed by the invention into the washing or rinsing water in a delayed release pattern so that there is always only a small concentration of active agents present. In this concentration,

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although the agents are effective in protecting glassware against corrosion, they are not present in a high enough concentration to lead to the undesirable formation of insoluble salts to any significant degree. The disadvantages of using insoluble zinc compounds described above are therefore also avoided by using the water-soluble glass proposed by the invention.

By using the water-soluble glass proposed by the invention in ground form as an additive to standard dishwasher products, which are generally made as powders or liquids, the problem of separation described above is also resolved since the use of a water-soluble glass offers greater flexibility in terms of adjusting the specific density to requirements.

If the water-soluble glass proposed by the invention is provided in tablet form and placed in the interior of the dishwasher at a point which is accessible to the washing and/or rinsing water, e.g. in the cutlery basket, it will also provide, for the first time ever, active protection against corrosion throughout all washing and rinsing cycles, i.e. from the pre-rinse cycle through to the cleaning cycle and then the intermediate rinse cycles through to the final rinse cycle and, what is more, will last for several cycles. As a result, not only is glassware thoroughly protected against corrosion in the dishwasher, handling is made significantly easier and more convenient for the consumer.

The glasses proposed by the invention may be produced by melting mixtures of the oxide components or precursors thereof for a sufficient time to obtain a homogeneous melt, which is then cooled until it solidifies.

The tablets may be made using various methods, for example by casting (e.g. in a graphite mould), drawing, pressing or blowing.

If the glass proposed by the invention is used in crushed form, it may be ground in a grinder specifically suited to this purpose, for example, and an appropriate fraction of particles separated out, e.g. having an average particle size of at most 500 μm . However, particulate glass may also be produced by other methods, e.g. by breaking down thin glass discs, resulting in disc-shaped, thin platelets which may be up to several millimeters in diameter. Both embodiments, i.e. spherical particles with a specific maximum particle size and thin platelets, will reliably ensure thorough mixing with the dishwasher detergent and prevent separation during storage and transportation.

The solubility of the glass used is defined in accordance with DIN ISO 719. This test method tests glass as a material and is conducted on glass fines. Grains of a size of between 300 and 500 μm are extracted from 2 g of fines over a period of 60 min with water conforming to Quality 2 at 98° C. Further details of how the test is conducted can be found in the relevant standard. However, by contrast with the aforementioned standard, the degree of solubility is determined not by titration with acid but by a standard gravimetric definition of the mass loss.

EXAMPLE 1

In this example, a glass of the following composition was produced, using the method outlined below:

TABLE 1

Component	Molar %
P_2O_5	20
ZnO	36

TABLE 1-continued

Component	Molar %
SO ₃	20
Na ₂ O	10
Li ₂ O	5
K ₂ O	7
CaO	2

Ammonium compounds or carbonates of the respective elements were used as raw materials and the sulphate was incorporated by adding 20 molar % of zinc sulphate. The raw materials were mixed and melted in an aluminum oxide pan in oven electrically heated to 850° C. After a residence time of 3 h, the glass was poured out.

In order to produce an appropriate powder, the drained glass was cooled in air, ground with an impact cross-blade mill and screened to obtain a grain fraction with a mean particle size of less than 400 μ m.

In order to produce a solid glass tablet, the hot glass was poured into a graphite mould and then cooled slowly in an annealing furnace starting at 300° C.

The resultant zinc phosphate glass has a solubility characterized by a mass loss of 75 mg under the conditions specified in DIN ISO 719.

The following comparative tests were conducted to ascertain the effectiveness of the glass proposed by the invention as a corrosion inhibitor for glassware in dishwashing machines. In a first series of tests, test glasses were rinsed 50 and 100 times in a special long-running dishwashing machine (Miele G540 Spezial). Powdered dishwasher detergent, Calgonit® Ultra 2-phase powder, was used as a reference substance. The comparative tests were conducted using the powdered or gel dishwasher detergent to which was added, by admixing or stirring, 1% by weight of the glass proposed by the invention in powdered form.

Another series of tests was conducted using the reference dishwasher detergent whilst simultaneously placing a solid block made from the glass proposed by the invention, the dimensions of which (prior to the test cycles) were 30 mm×30 mm×5 mm, in the cutlery basket of the dishwashing machine. The weight loss of the solid glass block after 100 rinsing cycles was approximately 22.5 g.

Dose of detergent: 20 g Calgonit® Ultra 2-phase powder per rinse cycle, automatically metered at the start of the washing cycle.

Water hardness in the machine: 0.1° dGH, central softening by means of an ion exchanger, internal ion exchanger not in operation.

Washing programme: 65° C. programme, i.e. (both the washing and the clear rinse cycle were run at 65° C.).

Water consumption per rinse cycle: 23.5 l.

Quantity of rinsing agent per cycle: 3 ml (Calgonit® rinsing agent).

The glasses were not soiled, in addition to test glasses, blind glasses were placed in the washing baskets.

The test objects consisted of the following types of glass:

Schott Zwiesel Glaswerke AG:

“Neckarbecher” 1812/2, wine glass, crystal glass

“Paris” 4858/42, large tumblers, crystal glass

Nachtmann Bleikristallwerke GmbH:

“Opal”, whisky glass; lead crystal glass

“Bistro”, whisky shot, lead crystal glass

Verrerie Cristallerie D'Arques:

“Luminarc Octime Transparent”, 30 cl whisky glass,

“Luminarc Islande Dauphine”, decorated large tumbler.

The weight loss of the test glasses after 50 and 100 rinsing cycles was gravimetrically determined. Perceptible changes in the glass surface were evaluated in daylight and in a special illuminated box. The illuminated box is a box with dimensions of 70 cm×40 cm×65 cm (L×B×H), the entire interior of which is painted matt black. The box is illuminated above with an Osram I. 20 W/25 S lamp (60 cm in length), which is covered with a screen to the front. Racks are arranged in the box, on which the glasses can be placed. The front of the box is open.

The glass corrosion was visually assessed using the following scale:

Evaluation	Damage in daylight	Damage in illuminated box
0	No change	No change
1	No visible clouding	Slight clouding
2	Barely any visible clouding	Clearly visible clouding
3	Readily visible clouding	Strong clouding
4	Significant damage, glass unsightly	—

The results of the series of tests, based on an investigation of the effect of adding 1% by weight of the ground glass described above or placing it in the dishwashing machine as a solid glass block, as compared with the powdered reference dishwasher detergent, are set out in Tables 2a to 2e below.

Adding 1% of ground glass corresponds to the addition of approximately 0.35% of zinc oxide, since the corresponding glass contains approximately 1/3 zinc oxide.

As stated above, the weight loss of the solid glass block after 100 rinse cycles was approximately 22.5 g. From this, it can be calculated that the average weight loss per rinsing cycle is 225 mg. Based on a detergent dose of 20 g of powder and taking account of the fact that the glass contains approximately 1/3 zinc oxide, the quantity of zinc oxide added per rinsing cycle can be calculated as being 0.4%. Accordingly, approximately the same quantity of zinc oxide is released per rinsing cycle by adding 1% of ground glass or using the solid glass block.

TABLE 2a

Mass loss			
	Reference	1% ground glass	Solid glass
50 rinse cycles			
Neckar	38	23	10.5
Paris	57.5	36	25
Octime	28	24	14.5
Islande Dekor	561	223	122
100 rinse cycles			
Neckar	83	33	24
Paris	130.5	53.5	38.5
Octime	60	29	20.5
Islande Dekor	1,093	474	308

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TABLE 2b

<u>Glass damage</u>			
	Reference	1% ground glass	Solid glass
<u>50 rinse cycles</u>			
Neckar	3.0	1.5	1.0
Paris	2.0	0	0.5
Oetime	5.5	1.0	0
Islande Dekor	4.0	1.0	1.0
<u>100 rinse cycles</u>			
Neckar	2.5	2.5	1
Paris	2.5	0	0.5
Oetime	11.5	4.5	4.5
Islande Dekor	8.5	4	3

TABLE 2c

List of glass damage		
Reference	50 rinse cycles	100 rinse cycles
Glasses		
Neckarbecher	GTk 2, GTm 1	GTk 1-2, GTm 1
Paris (large)	GTc 2	GTc 2-3
Oetime	GTm 1-2, GTk 1-2	GTm 3, GTk 3, CLk 3, CLc 2-3
Islande Dekor	FA 1, DS 2, CLc 1	FA 3, DS 3-4, CLc 2

TABLE 2d

List of glass damage		
With 1% glass powder	50 rinse cycles	100 rinse cycles
Glasses		
Neckarbecher	GTk 1, GTm 0-1	GTk 1-2, GTm 1
Paris (large)	0	0
Oetime	CLk 1	GTm 1, GTk 1-2 CLk 2
Islande Dekor	DS 1	DS 2, FA 2

TABLE 2e

List of glass damage		
Solid glass	50 rinse cycles	100 rinse cycles
Glasses		
Neckarbecher	GTk 1	GTk 1
Paris (large)	GTk 0-1	GTk 0-1
Oetime	0	GTm 1-2, GTk 2, CLk 1
Islande Dekor	0	DS 1-2, FA 1-2

GT = Glass clouding
 m = Mouth edge area
 CL = thin parallel streaking, "Cordlines"
 k = Glass bowl
 FA = Colour changes
 s = Stein
 DS = Decoration damage
 f = Glass base
 e = Glass crackling

As may be seen from the tables, both adding 1% of ground glass and providing the solid glass block significantly improves protection against corrosion as compared with the reference composition, the protection afforded by the solid glass block being significantly better than that obtained by adding ground glass.

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In another series of tests, the glass proposed by the invention was compared with the insoluble zinc oxide and not readily soluble zinc phosphate known from the prior art. In these instances, the detergent used was Calgonit® Ultra 2-phase gel (25 ml per rinse cycle). From Table 3a below, it may be seen that the protective effect against corrosion measured by mass loss in accordance with the method described above, obtained by adding 1% by weight of the glass proposed by the invention in this example corresponds to adding 0.5% of zinc oxide. However, since the zinc oxide content in the corresponding glass is only about 1/3, which means that the addition of 1% glass corresponds to about only 0.35% zinc oxide, the anti-corrosion effect produced by the glass proposed by the invention is surprisingly higher than that obtained simply by adding zinc oxide and is also superior to the effect obtained by adding an even higher concentration of zinc phosphate, expressed as ZnO.

TABLE 3a

Mass loss				
	100 rinse cycles 0.25% ZnO	1% glass	0.5% ZnO	1% Zn-Phos. (=0.63% ZnO)
Neckarbecher	22	14	12	20
Paris (large)	21	16	10	17
	36	18	21	38
	34	14	25	27
Opal	36	30	25	33
Bistro	42	34	34	33
Total	191	126	127	168

TABLE 3b

Glass damage				
	100 rinse cycles 0.25% ZnO	1% glass	0.5% ZnO	1% Zn-Phos. (=0.63% ZnO)
Neckarbecher	GTk 1; MR 1	GTk 0-1	GTk 0-1	GTk 2, GTm 2
Paris (large)	GTc 1	0	0	0
Opal	0	0	0	0
Bistro	0	0	0	0

GT = Glass clouding
 m = Mouth edge area
 CL = thin parallel streaking, "Cordlines"
 k = Glass bowl
 FA = Colour changes
 s = Stein
 DS = Decoration damage
 f = Glass base
 e = Glass crackling

EXAMPLE 2

In this example, a glass of the following composition was made using the same method as that described with reference to example 1:

TABLE 4

Component	Molar %
P ₂ O ₅	20
Na ₂ O	9.5
K ₂ O	12
CaO	38
SiO ₂	20.5

Initial tests on the effectiveness of the glass proposed by the invention as a glass corrosion inhibitor in dishwasher

machines showed positive results similar to those obtained using the glass described in example 1.

EXAMPLE 3

In this example, a glass of the following composition was made using the same method as that described with reference to example 1:

TABLE 5

Component	Molar %
P ₂ O ₅	40.5
Na ₂ O	20.3
CaO	10.7
Al ₂ O ₃	8
SO ₃	20.5

Initial tests on the effectiveness of the glass proposed by the invention as a glass corrosion inhibitor in dishwasher machines showed positive results similar to those obtained using the glass described in example 1.

The features of the invention disclosed in the description above and in the claims and drawings may be used individually or in any combination to apply the invention in its different embodiments.

What is claimed is:

1. A method for inhibiting corrosion of glassware in a dishwashing machine, which method comprises bringing said glassware into contact, during a washing and/or rinsing cycle of the dishwashing machine, with a water-soluble glass comprising at least one glass-forming component, and at least one compound which releases an active anti-corrosion agent, each of the at least one compound accounts for no more than 85 molar percent of the glass, and a solubility of the water-soluble glass is defined by a mass loss of at least 0.5 mg following hydrolysis under conditions specified in DIN ISO 719.
2. The method according to claim 1 wherein the solubility of the water-soluble glass is defined by a mass loss of at least 10 mg following hydrolysis under the conditions specified in DIN ISO 719.
3. The method according to claim 2 wherein the solubility of the water-soluble glass is defined by a mass loss of at least 50 mg following hydrolysis under the conditions specified in DIN ISO 719.
4. The method according to claim 1 wherein the at least one compound which releases an active anti-corrosion agent is selected from the group consisting of oxides of zinc, aluminum, tin, magnesium, calcium, strontium, titanium, zirconium, manganese, lanthanum, mixtures thereof and precursors thereof.
5. The method according to claim 4 wherein the at least one compound which releases an active anti-corrosion agent comprises zinc oxide or a precursor thereof.
6. The method according to claim 1 wherein the at least one glass-forming component comprises phosphorus pentoxide or a precursor thereof.
7. The method according to claim 1 wherein the at least one glass-forming component is selected from the group consisting of alkali metal oxides and precursors thereof.
8. The method according to claim 1 wherein the water-soluble glass is used in a form of a tablet.
9. The method according to claim 8 wherein the tablet is made by casting or drawing the water-soluble glass.
10. The method according to claim 1 wherein the water-soluble glass is used in a ground form.
11. The method according to claim 10 wherein the ground glass has a mean particle size of at most 500 μm .

12. The method according to claim 1 wherein the water-soluble glass is used in a form obtained by breaking down thin glass discs.

13. A composition for use in a dishwashing machine to protect glassware from corrosion, which composition contains a quantity of a water-soluble glass in a crushed form, wherein the water-soluble glass consists essentially of at least one glass-forming component and at least one compound which releases an active anti-corrosion agent during a washing and/or rinsing cycle of the dishwashing machine, each of the at least one compound accounts for at most 85 molar percent of the glass, and a solubility of the water-soluble glass is defined by a mass loss of at least 0.5 mg following hydrolysis under the conditions specified in DIN ISO 719.

14. The composition according to claim 13 wherein the crushed, water-soluble glass is present in a quantity of from 0.1 to 10.0% by weight.

15. The composition according to claim 14 wherein the crushed, water-soluble glass is present in a quantity of from 0.5 to 5.0% by weight.

16. The composition according to claim 13 wherein the water-soluble glass is in a form of thin glass platelets.

17. The composition according to claim 13 wherein the water-soluble glass is in a ground form.

18. The composition according to claim 17 wherein the ground glass has a mean particle size of at most 500 μm .

19. A composition for use in a dishwashing machine to protect glassware from corrosion, which composition contains a quantity of a water-soluble glass in a tablet form, wherein the water-soluble glass consists essentially of at least one glass-forming component and at least one compound which releases an active anti-corrosion agent during a washing and/or rinsing cycle of the dishwashing machine, each of the at least one compound accounts for at most 85 molar percent of the glass, and a solubility of the water-soluble glass is defined by a mass loss of at least 0.5 mg following hydrolysis under the conditions specified in DIN ISO 719.

20. The composition according to claim 19 wherein the tablet is made by casting or drawing the water-soluble glass.

21. The composition according to claim 13 or 19 wherein the solubility of the water-soluble glass is defined by a mass loss of at least 10 mg following hydrolysis under the conditions specified in DIN ISO 719.

22. The composition according to claim 21 wherein the solubility of the water-soluble glass is defined by a mass loss of at least 50 mg following hydrolysis under the conditions specified in DIN ISO 719.

23. The composition according to claim 13 or 19 wherein the at least one compound which releases an active anti-corrosion agent is selected from the group consisting of oxides of zinc, aluminum, tin, magnesium, calcium, strontium, titanium, zirconium, manganese, lanthanum, mixtures thereof and precursors thereof.

24. The composition according to claim 23 wherein the at least one compound which releases an active anti-corrosion agent is zinc oxide or a precursor thereof.

25. The composition according to claim 13 or 19 wherein the at least one glass-forming component is phosphorus pentoxide or a precursor thereof.

26. The composition according to claim 13 or 19 wherein the at least one glass-forming component is selected from the group consisting of alkali metal oxides and precursors thereof.

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